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(54) DECOMPOSITION TREATMENT METHOD OF FLUORINE-CONTAINING COMPOUND, CATALYST AND DECOMPOSITION TREATMENT DEVICE

(57)Abstract:

PROBLEM TO BE SOLVED: To efficiently decompose and treat fluorine compounds containing only fluorine as halogen such as CF₄ and C₂F₆.

SOLUTION: In the method for decomposing and treating fluorine-containing compounds, gas flow consisting of fluorine compounds containing only fluorine as halogen is brought into contact with an Al-containing catalyst such as a catalyst consisting of Al and Ni, Al and Zn, Al and Ti at about 200-800°C in the existence of steam and fluorine contained in the gas flow and fluorine contained in gas flow is converted into hydrogen fluoride. Further, the device for decomposing and treating the fluorine-containing compounds is equipped with a reactor 15 filled with the catalyst 14 containing Al, a water adding vessel in which steam is added to gas flow containing a compound consisting of fluorine and one of

carbon, sulfur and nitrogen treated in the reactor 15 and a heating means consisting of a preheater 12 and a heater 13 by which one hand of the catalyst 14 filled in the reactor 15 and the gas flow containing fluorine compounds 1 introduced into the reactor 15 is heated at such temperature that the fluorine compounds 1 are hydrolyzed.

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CLAIMS

[Claim(s)]

[Claim 1] The decomposition art of the fluorine content compound characterized by contacting the gas stream which contains this fluorine with a compound with the element chosen from carbon, nitrogen, and sulfur including a fluorine as a halogen at the catalyst and the temperature of about 200-800 degrees C which come to contain aluminum under existence of a steam, hydrolyzing the fluorine compound in said gas stream, and converting into hydrogen fluoride.

[Claim 2] The decomposition art of the fluorine content compound characterized by making the catalyst containing at least one chosen from in the gas stream containing said fluorine compound in claim 1 including aluminum among Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, Si, and Pt touch.

[Claim 3] The decomposition art of the fluorine content compound characterized by said catalyst containing S further in an approach according to claim 2.

[Claim 4] The decomposition art of the fluorine content compound characterized by containing the component which constitutes said catalyst in an approach according to claim 2 in the state of an oxide component independent [each] or the multiple oxide of aluminum and other components.

[Claim 5] At least one of the fluorine compounds with which the gas stream containing said fluorine compound consists of CF4, CHF3, C2F6, C3F8, C4F8, and C5F8 in an approach according to claim 1 is included, and it is this fluorine compound CO and CO2 Decomposition art of the fluorine content compound characterized by reaching on the other hand at least, and decomposing into HF.

[Claim 6] The gas stream which contains said fluorine compound in claim 1 is SF6. The becoming fluorine compound is included and it is this SF6. Decomposition art of the fluorine content compound characterized by for SO2 and SO3 reaching on the other hand at least, and decomposing into HF.

[Claim 7] The gas stream which contains said fluorine compound in claim 1 is NF3. The becoming fluorine compound is included and it is this NF3. Decomposition art of the fluorine content compound characterized by for NO, NO2, and N2O reaching on the other hand at least, and decomposing into HF.

[Claim 8] The gas stream which contains this fluorine as a halogen with a compound with the element chosen from carbon, nitrogen, and sulfur including a fluorine under existence of a steam Make it contact at the catalyst and the temperature of about 200-800 degrees C which come to contain aluminum, hydrolyze the fluorine compound in said gas stream, and it converts into hydrogen fluoride. Then, the decomposition art of the fluorine content compound characterized by neutralizing with alkali the water which the gas stream containing this hydrogen fluoride is contacted in water, removes hydrogen fluoride, and contains this hydrogen fluoride.

[Claim 9] The catalyst for decomposition processing of the fluorine content compound

which is the catalyst used in order to hydrolyze the halogenated compound which contains only a fluorine as a halogen, and is characterized by coming to contain aluminum oxide.

[Claim 10] It consists of aluminum and at least one chosen from among Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, Si, and Pt in claim 9. The catalyst for decomposition processing of the fluorine content compound with which aluminum is [the atomic ratio of aluminum:M (M is at least one of Zn, nickel, Ti, Fe, Sn, Co Zr, Ce, and the Si)] 50-99-mol %, and M is characterized by 50-1-mol being %.

[Claim 11] The catalyst for decomposition processing of the fluorine content compound characterized by including S 0.1 to 20% of the weight further in a catalyst according to claim 10.

[Claim 12] The catalyst for decomposition processing of the fluorine content compound characterized by said each component existing in the state of an oxide component independent [each] or the multiple oxide of aluminum and other components in a catalyst according to claim 10.

[Claim 13] The catalyst for decomposition processing of the fluorine content compound characterized by consisting of aluminum and Pt and including Pt 0.1 to 2% of the weight in a catalyst according to claim 10.

[Claim 14] The water addition machine which adds a steam to the gas stream containing the reactor filled up with the catalyst which comes to contain aluminum, the fluorine processed with this reactor, carbon, sulfur, and one compound of nitrogen, The decomposition processor of the fluorine content compound characterized by having a heating means for heating to the temperature to which a fluorine compound may hydrolyze at least one side of the fluorine compound content gas stream introduced into the catalyst and this reactor with which this reactor was filled up.

[Claim 15] The decomposition processor of the fluorine content compound characterized by having an exhaust gas cleaning tank for washing with water the gas stream discharged by the latter part of said reactor from this reactor in equipment according to claim 14.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to a decomposition processor at the approach and catalyst list which carry out decomposition processing of the compound which contains a fluorine as a halogen like CF₄, C₂F₆, and SF₆ and NF₃ efficiently at

low temperature.

[0002]

[Description of the Prior Art] The fluorine compound gas which contains only a fluorine as a halogen like CF₄, C₂F₆, and SF₆ and NF₃ is used for the semi-conductor etching agent, the semi-conductor cleaning agent, etc. by the large quantity. However, when these matter was emitted into atmospheric air, it became clear that warming of the earth was caused.

[0003] Gas, such as CF₄, C₂F₆, and SF₆, NF₃, contains many fluorines (F) as a molecule constituent. Electronegativity of a fluorine is the highest of all elements, and it forms the chemical very stable matter. CF₄, C₂F₆, etc. have the especially strong intramolecular force, and it is the matter lacking in reactivity. It is necessary to heat to an elevated temperature, and the energy of a large quantity is consumed from this property to decompose by combustion etc. Moreover, the decomposition reaction in an elevated temperature has the large corrosion rate of the equipment ingredient by gas, such as hydrogen fluoride to generate, and the actual condition is that there is no suitable decomposition art.

[0004] As a decomposition art, current and being proposed are the combustion technologies in an elevated temperature. However, in order to use combustible gas, such as a propane, by this approach, it is CO₂ of a large quantity by combustion. And NO_x which is harmful matter generates. Moreover, in order to use combustible gas, such as a propane, there is danger of explosion. Moreover, since it burns at about 1000 degrees C, with the corrosive gas generated by disassembly of a halogenated compound, a furnace wall is damaged, the frequency of a maintenance becomes high, and operation cost becomes large. Therefore, the technique which is low temperature more, and can be decomposed without generating harmful matter is required.

[0005] Although it applies for patents various until now about the decomposition catalyst of a halogenated compound, there are few reports of having disassembled the halogenated compound which contains only a fluorine as a halogen which is object gas of this invention. CF₄ which contains only a fluorine as a halogen although hydrolysis of the halogenated compound by the catalyst containing a titania is indicated by JP,3-66388,A It is described that it receives and resolvability ability is not shown. Moreover, although it tried to hydrolyze CFC-14 (CF₄) using the 2O₃/activated carbon of Fe(s), Okazaki and others was not decomposed as indicated by Chem.Lett.pp(1989).1901-1904. It is extent it is reported about disassembly of the fluorine compound which contains only a fluorine as a halogen that the example using the decomposition agent which becomes JP,7-116466,A from a hydrogen fluoride processing inorganic oxide is.

[0006]

[Problem(s) to be Solved by the Invention] The object of this invention offers CF₄, C₂F₆, the decomposition art that disassembles efficiently the fluorine compound which contains only a fluorine as a halogen like SF₆ and NF₃ at low temperature, high cracking severity and a decomposition catalyst with a long catalyst life, and a decomposition processor.

[0007]

[Means for Solving the Problem] this invention persons resulted in this invention, as a result of advancing examination of the decomposition art which is low temperature, and can be efficient, and can disassemble the compound which contains only a fluorine as a halogen like CF₄, C₂F₆, and SF₆ and NF₃, and corrosion of the equipment by the

corrosive gas in cracked gas cannot produce easily to a detail.

[0008] That is, only the fluorine was contained as a halogen, the gas stream which contains this fluorine with a compound with the element chosen from carbon, sulfur, and nitrogen was contacted at the catalyst which comes to contain aluminum under existence of a steam, and about 200-800 degrees C, said fluorine compound was hydrolyzed, and the approach of converting said fluorine compound in a gas stream into hydrogen fluoride was found out.

[0009] CF₄ which is object gas, and the halogenated compound which contains only a fluorine as a halogen like C₂F₆ grade have the property of a fluorine with high electronegativity to the strong intramolecular force, is the reactant scarce matter, and is hardly disassembled at a reaction with oxygen. That is, high cracking severity is acquired only after adding H₂O.

[0010] The fluorine compound made into the object of this invention is a halogenated compound which contains only a fluorine as a halogen. As a constituent of a compound, they are a fluorine, carbon, oxygen, sulfur, nitrogen, etc. As an example of a compound, they are CF₄, CHF₃, CH₂F₂, CH₃F, C₂F₆, C₂HF₅, C₂H₂F₄, C₂H₃F₃, C₂H₄F₂, C₂H₅F, C₃F₈, CH₃OCF₂CF₃, C₄F₈, C₅F₈, SF₆, and NF₃ grade.

[0011] The catalyst which comes to contain aluminum is used in the fluorine compound decomposition art of this invention. aluminum is used in the form of an oxide. Although aluminum can be used independently, it can use combining at least 1 component of Zn, nickel, Ti, Fe, Sn, Pt, Co, Zr, Ce, and the Si. Furthermore, S can be added for these catalysts and the decomposition activity of a catalyst can be raised to them.

[0012] The thing which is the need as catalyst engine performance is having high cracking severity and a long catalyst life. As a result of examining in a detail the catalyst which shows these engine performance, it found out that high resolvability ability could be given with the raw material which also uses 2Oaluminum3 simple substance.

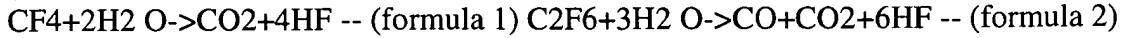
[0013] Cracking severity can be raised rather than the case where aluminum is used independently, by using the catalyst which consists of aluminum and at least 1 component of Zn, nickel, Ti, Fe, Sn, Pt, Co, Zr, Ce, and the Si. In these catalysts, aluminum exists in the state of aluminum 2O₃ or the added metal component, and a multiple oxide. Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, and Si exist in the state of an oxide or a multiple oxide with aluminum. With these catalysts, it is desirable that aluminum is [M] 50-1-mol % at 50-99-mol % for the atomic ratio of aluminum:M (= at least one of Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, and the Si). or the catalyst which consists of aluminum and Pt -- setting -- Pt -- 0.1 - 2wt% -- containing is desirable. High cracking severity is acquired by making the amount of addition components other than aluminum into said within the limits.

[0014] It is effective in acquiring a long catalyst life to control crystallization of aluminum 2O₃ in a catalyst, and it is desirable to multiple-oxide-ize the metal component which contained nickel, Zn, etc. and was added like NiAl 2O₄ and ZnAl 2O₄, and aluminum. As the approach of the improvement in the catalyst engine performance, the approach of adding S is in a catalyst. The approach of using a sulfate at the time of catalyst preparation, or using a sulfuric acid for it as the addition approach of S, is applicable. S in a catalyst is SO₄. It exists in the form of ion etc. and serves to strengthen the quality of acidity of a catalyst. The amount of S has 0.1 - 20 desirable % of the weight.

[0015] In the decomposition art of this invention, oxygen may be added in the gas stream containing fluorine compounds, such as CF₄ and C₂F₆. It can use for oxidation reaction of CO in cracked gas etc.

[0016] There is the following in the typical reaction of the decomposition reaction of a fluorine compound.

[0017]


$$\text{C}_2\text{F}_6 + 3\text{H}_2\text{O} \rightarrow \text{CO} + \text{CO}_2 + 6\text{HF} \quad (\text{formula 2})$$

CHF₃ + H₂O → CO + 3HF -- (formula 3) If oxygen exists since the catalyst of this invention also has CO oxidation engine performance although CO generates at the reaction which reaches (formula 3) (formula 2), it will be CO₂ about CO. It can carry out.

[0018] It is necessary to adjust the amount of the steam to add so that a hydrogen molecule equivalent to the F number in the fluorine compound to process at least may exist. Thereby, the fluorine in a compound can be converted into hydrogen fluoride, and it is made to the gestalt which is easy to carry out after treatment.

[0019] The reaction temperature which hydrolyzes a fluorine compound has desirable about 200-800 degrees C. The reaction temperature in the case of processing the fluorine compound which consists of carbon, a fluorine, and hydrogen at least has desirable about 500-800 degrees C. Degradation of a catalyst is quick, although the rate of superresolution will be obtained if it is used at the elevated temperature beyond this.

Moreover, the corrosion of an equipment ingredient becomes easy to progress. In contacting for a catalyst the gas stream which contains only a fluorine as a halogen and contains this fluorine with a compound with the element chosen from carbon, sulfur, and nitrogen, it is 0.1 - 3vol% to make the content of the fluorine compound in a gas stream into 0.1 - 10vol% desirable still more preferably. Moreover, space velocity is 100 per-hour -10,000. Per hour is desirable still more desirable and it is 100 per-hour -3,000. It is per hour. Space velocity (h⁻¹) is called for in a reactant gas flow rate (ml/h) / the amount of catalysts (ml).

[0020] In the fluorine compound decomposition art by this invention, hydrogen fluoride, a carbon dioxide, etc. generate as a decomposition product. the sulfur oxide of SO₂ and SO₃ grade, and NO and NO₂ etc. -- nitrogen oxides may generate [in addition,] In order to remove these decomposition products, it is desirable for an alkali solution to wash or to wash with water. The approach of washing with water is desirable as an approach of removing hydrogen fluoride, controlling the corrosion of equipment. However, it is desirable to neutralize the water containing hydrogen fluoride with alkali after that in the case of backwashing by water. As alkali, common alkali reagents, such as a water solution of a calcium hydroxide or a sodium hydroxide and slurry liquid, can be used.

[0021] As an aluminum raw material for preparing the catalyst of this invention, the mixture of gamma-alumina, gamma-alumina, and delta alumina etc. can be used. What formed the oxide by baking shows high decomposition activity, using especially boehmite as an aluminum raw material.

[0022] A nitrate, a sulfate, ammonium salt, a chloride, etc. can be used as a raw material of the various metal components for preparing the catalyst of this invention. Nickel nitrate, a nickel sulfate, etc. can be used as a nickel raw material. These hydrates can also be used. Sulfuric-acid titanium, a titania sol, etc. can be used as a Ti raw material.

[0023] The manufacturing method of the catalyst of this invention can use all, such as settling used for manufacture of the usual catalyst, an impregnation method, and the

kneading method.

[0024] Moreover, the catalyst in this invention can be used, fabricating it a grain, in the shape of a honeycomb, etc. as it is. As a fabricating method, the approach of arbitration is employable according to the objects, such as an extrusion-molding method, the making tablet fabricating method, and the rolling corning method. Moreover, it can also be used, being able to coat the honeycomb and plate made from a ceramic metallurgy group.

[0025] Although the reactor used in order to enforce the art of this invention is easy to be the thing of the usual fixed bed, the moving bed, or a fluid bed mold, since corrosive gas, such as HF, occurs as decomposition generation gas, it should constitute the reactor from an ingredient which is hard to damage by these corrosive gas.

[0026] The processor used in order to enforce the art of this invention A means to supply nitrogen, air, or oxygen to the means, for example, the gas stream, which adjusts the concentration of the fluorine compound in a gas stream other than the above-mentioned reactor, A means to heat at least one side in order to contact a gas stream and said catalyst at the temperature of 200-800 degrees C, A means to add a steam or water to said gas stream in order to disassemble said fluorine compound, When said gas stream contacts the catalyst with which said reactor was filled up the generated decomposition product -- water and/, or an alkali water solution -- washing -- some carbon dioxides in this decomposition product, some sulfur oxides of SO₂ and SO₃ grade, NO, and NO₂ etc. -- the exhaust gas cleaning tank from which the part and hydrogen fluoride of nitrogen oxides are removed is provided. It is still more desirable to establish a means to adsorb with an adsorbent etc. the carbon monoxide in said decomposition product which was not removed in the latter part of an exhaust gas cleaning tank, a sulfur oxide, and nitrogen oxides.

[0027] The art of the fluorine compound content gas of this invention is also applicable to an established chip fabrication factory. since there is generally flue-gas-treatment equipment of acid component gas in a chip fabrication factory -- this -- using -- the catalyst of this invention -- CF₄ etc. -- it installs in the exhaust gas line of a fluorine compound, and if a steam is added and heated, decomposition processing of the fluorine compound can be carried out. Moreover, it can move to the location in which the whole equipment or a part of this invention was loaded into the truck etc., and the discarded fluorine compound stuffing bomb is stored, and the contained fluorine compound can also be extracted and processed directly. Moreover, the exhaust gas adsorption tub which adsorbs the circulating pump which circulates through the penetrant remover in an exhaust gas cleaning tank, the carbon monoxide in exhaust gas, etc. may be carried simultaneously. Moreover, a generator etc. may be carried.

[0028] According to the decomposition art of the fluorine compound of this invention, a fluorine compound can be disassembled at low temperature and operation cost can be reduced.

[0029] When processing fluorine compound content gas, the corrosion of the equipment ingredient by acid components, such as HF decomposed and generated, poses a problem, but according to this invention, since the temperature to be used is low temperature, a corrosion rate is small and can decrease the maintenance frequency of equipment.

[0030] The decomposition art of the fluorine compound of this invention consists of an exhaust gas washing process which carries out neutralization clearance of the acid component in the catalytic-reaction process which disassembles a fluorine compound,

and decomposition generation gas, and can miniaturize equipment.

[0031] In order to base disassembly of a fluorine compound on a reaction with a steam, its safety as a decomposition art is high, and it does not have danger, such as explosion, like [at the time of using combustible gas].

[0032]

[Embodiment of the Invention] Hereafter, an example explains this invention to a detail further. This invention is not limited only to these examples.

[0033] Drawing 1 shows an example of the decomposition treatment process of the halogenated compound in the case of using at a semi-conductor etching process.

[0034] the inside of the etching furnace decompressed at the etching process -- CF4 etc. - - a fluorine compound 1 is put in, and it excites for 20 minutes with the plasma, and is made to react with a semi-conductor The inside of a chamber was permuted by N22 after that, the concentration of a halogenated compound was diluted to several%, and it has discharged out of an etching furnace by about 10 l/min.

[0035] this emission gas -- air 3 -- adding -- CF4 etc. -- the halogenated compound was diluted. Nitrogen may be added and diluted at this time. Moreover, nitrogen and oxygen may be added and diluted. The reactant gas 5 which added the steam with the water addition vessel 4 further to this dilution gas is sent to a decomposition process. A decomposition process is performed using the reactor filled up with the catalyst. The concentration of the halogenated compound in reactant gas is about 0.5 - 1%. In a decomposition process, reactant gas 5 is contacted at the catalyst which comes to contain aluminum on condition that space-velocity 1,000 per hour (space velocity (h-1) = a reactant gas flow rate (ml/h) / the amount of catalysts (ml)), and about 200-800 degrees C. In this case, reactant gas may be heated and a catalyst may be heated with an electric furnace etc. Cracked gas 6 is sent to an exhaust gas washing process. At an exhaust gas washing process, the spray of the water 7 is carried out to cracked gas 6, and the exhaust gas 8 with which the acid component in cracked gas was removed is emitted out of a system. The acid wastewater 9 containing a sour gas is processed with a chip fabrication factory existing waste-water-treatment facility. CF4 etc. -- the cracking severity of a halogenated compound analyzes reactant gas 5 and cracked gas 6 using a FID (abbreviated name of Flame Ionization Detector) gas chromatograph, and a TCD (abbreviated name of ThermalConductivity Detector) gas chromatograph, and asks for them by the material balance of an inlet port and an outlet.

[0036] An example of the processor of this invention is shown in drawing 10 . water carries out the spray of the fluorine compound gas from an etching process by the inlet-port spray 10 -- having -- SiF4 in gas etc. -- an impurity is removed. This gas and the water 7 refined in air 3 and ion-exchange-resin 11 grade are heated at a heater 13 within a preheater 12. A reactor 15 is filled up with the catalyst 14 containing aluminum. Moreover, it had the cooling room 17 which has the spray means 16 of water, and the spray means 18 of water in the latter part of a reactor 15, and it is equipped with the exhaust gas cleaning tank 20 containing a filler 19. Exhaust gas 8 is led by the blower 21 and the acid wastewater 9 is led with a pump 22. In addition, ion exchange treatment is carried out and the water containing the hydrogen fluoride of an exhaust gas cleaning tank can be reused as a pure-water raw material.

[0037] (Example 1) This example is an example which investigated the activity of various fluorine compound decomposition catalysts.

[0038] Air was added and diluted in C₂F₆ gas of 99% or more of purity. To this dilution gas, the steam was added further. The steam supplied pure water to the coil upper part using the micro tube pump, and made it gasify by about 0.2 ml/min. C₂F₆ concentration in reactant gas was about 0.5%. The catalyst and space velocity 2,000 which warmed this reactant gas from the coil exterior to predetermined temperature with the electric furnace It was made to contact in per hour.

[0039] A coil is a coil with a bore of 32mm made from Inconel, has the catalyst bed in the center of a coil, and has the pyrometer tube with an outer diameter of 3mm made from Inconel inside. Bubbling of the decomposition generation gas which passed the catalyst bed was carried out into the calcium-fluoride solution, and it was emitted out of the system. The cracking severity of C₂F₆ was searched for by the degree type by the FID gas chromatograph and the TCD gas chromatograph.

[0040]

[Equation 1]

$$\text{分解率} = 1 - \frac{\text{出口のハロゲン化合物}}{\text{供給したハロゲン化合物}} \times 100 (\%) \quad \cdots (\text{数1})$$

[0041] The method of preparation of each catalyst with which the trial was presented in the above-mentioned conditions below is shown.

[0042] Catalyst 1; commercial boehmite powder was dried at 120 degrees C for 2 hours. It is 0.5 at 300 degrees C in 200g of this desiccation powder. Time amount baking was carried out, and further, burning temperature was raised to 700 degrees C, and was calcinated for 2 hours. The obtained powder was put into metal mold and compression molding was carried out by the pressure of 500 kgf/cm². A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst after completion consists of aluminum 2O₃.

[0043] Catalyst 2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 85.38g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Zn=91:9 (mol %) in the atomic ratio. This catalyst contains the multiple oxide of ZnAl 2O₄ other than aluminum oxide and Zn oxide.

[0044] Catalyst 3; commercial boehmite was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 50.99g of nickel-sulfate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:nickel=91:9 (mol %) in the atomic ratio. This catalyst contains aluminum oxide, nickel oxide, the multiple oxide of NiAl 2O₄, and an S acid ghost.

[0045] Catalyst 4; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 125.04g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst

presentation after completion was aluminum:nickel=91:9 (mol %) in the atomic ratio. This catalyst contains aluminum oxide, nickel oxide, and the multiple oxide of NiAl 2O4.

[0046] Catalyst 5; commercial boehmite powder was dried at 120 degrees C for 1 hour. 300g of this desiccation powder, 354.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 300g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Ti=91:9 (mol %) in the atomic ratio.

[0047] Catalyst 6; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 115.95g of iron nitrate 9 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Fe=91:9 (mol %) in the atomic ratio.

[0048] Catalyst 7; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is the 95.43g of the second tin hydrates of chlorination. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Sn=91:9 (mol %) in the atomic ratio.

[0049] Catalyst 8; commercial boehmite powder was dried at 120 degrees C for 1 hour. To 200g of this desiccation powder, the water solution which diluted 22.2g (Pt concentration 4.5wt%) of dinitrodiammine Pt(II) nitric-acid solutions with 200ml of pure water was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst after completion is Pt to 2O3100 % of the weight of aluminum 0.68 weight % It contained.

[0050] Catalyst 9; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 125.87g of cobalt nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Co=91:9 (mol %) in the atomic ratio.

[0051] Catalyst 10; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 76.70g of zirconium nitrate 2 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Zr=91:9 (mol %) in the atomic ratio.

[0052] Catalyst 11; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 124.62g of cerium-nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst

presentation after completion was aluminum:Ce=91:9 (mol %) in the atomic ratio.

[0053] Catalyst 12; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 20wt% silica sol 129.19g. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Si=91:9 (mol %) in the atomic ratio.

[0054] A test result with a reaction temperature [of the above-mentioned catalysts 1-12] of 700 degrees C is shown in drawing 2 . The decomposition activity of the catalyst which consists of a catalyst which consists of aluminum and Zn, and aluminum and nickel towers otherwise and is high. Subsequently, the decomposition activity of the catalyst which consists of aluminum and Ti is high. It is considered to be the effectiveness of S that a catalyst 3 has high activity rather than a catalyst 4.

[0055] (Example 2) This example is the result of preparing the catalyst to which the presentation of aluminum and nickel was changed using the same aluminum raw material as the catalyst 4 of an example 1, and nickel raw material, and investigating the decomposition activity of C2F6.

[0056] Catalyst 4-1; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 8.52g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=99:1 (mol %) in the atomic ratio.

[0057] Catalyst 4-2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 66.59g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=95:5 (mol %) in the atomic ratio.

[0058] Catalyst 4-3; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 210.82g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=80:20 (mol %) in the atomic ratio.

[0059] Catalyst 4-4; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 361.16g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=70:30 (mol %) in the atomic ratio.

[0060] Catalyst 4-5; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 562.1g of nickel nitrate 6 hydrates. It mixed, and it kneaded, adding water. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion

was aluminum:nickel=60:40 (mol %) in the atomic ratio.

[0061] C₂F₆ concentration was made into 2% for the activity of a catalyst 4 and a catalyst 4-1 to the catalyst 4-5, and it investigated by the same approach as an example 1 except having made the amount of the pure water to supply into about 0.4 ml/min. The cracking severity 6 hours after test initiation is shown in drawing 3. When mol % of nickel/(nickel+aluminum) is 20 -30-mol %, activity is the highest, and subsequently to the 5-40-mol time of %, activity is high.

[0062] (Example 3) This example prepares the catalyst to which the presentation of aluminum and Zn was changed using the same aluminum raw material as the catalyst 2 of an example 1, and Zn raw material, and investigates activity.

[0063] Catalyst 2-1; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 215.68g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=80:20 (mol %) in the atomic ratio.

[0064] Catalyst 2-2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 369.48g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=70:30 (mol %) in the atomic ratio.

[0065] Catalyst 2-3; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 126.65g of this desiccation powder, it is 96.39g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=85:15 (mol %) in the atomic ratio.

[0066] C₂F₆ concentration was made into 2% for the activity of a catalyst 2 and a catalyst 2-1 to the catalyst 2-3, and it investigated by the same approach as an example 1 except having made the amount of the pure water to supply into about 0.4 ml/min. The cracking severity 6 hours after test initiation is shown in drawing 4. Activity is the highest when mol % of nickel/(nickel+aluminum) is 10 -30-mol %.

[0067] (Example 4) This example is the result of changing reaction temperature and performing decomposition of CF₄, CHF₃, and C₂F₆. A test condition is space velocity 1,000. It is the same as that of an example 1 except having considered as per hour and having diluted the halogenated compound with nitrogen instead of air. The catalyst used the catalyst 4-3 in an example 2. The result of the trial with each reaction temperature is shown in drawing 5. The catalyst which consists of aluminum and nickel has high decomposition activity also to CHF₃ and CF₄. Moreover, to these fluorine compounds, it has activity even with the low high temperature of about 600 degrees C, and is especially CHF₃. It received, and when CHF₃ concentration in reactant gas was 0.1%, at least 300 degrees C decomposed 35%.

[0068] (Example 5) This example is the result of investigating the effect of the steam in decomposition of C₂F₆. A test condition is space velocity 1,000. Except having considered as per hour, it is the same as that of an example 1. The catalyst made reaction

temperature 700 degrees C using the catalyst 4 in an example 1. The trial supplied the steam 2 hours after reaction initiation, and suspended supply of a steam after that. It was begun again to supply a steam 5 hours after. The result of a trial is shown in drawing 6. Cracking severity increased at the time of addition of a steam, and decomposition of C₂F₆ became clear [being based on hydrolysis].

[0069] (Example 6) This example is the result of performing SF₆ and decomposition of C₃F₈ using the catalyst 4-3 which consists of aluminum and nickel. SF₆ A test condition is SF₆ of 99% or more of purity. It is the same as that of an example 1 except having considered as space-velocity 1,000 per hour, and having diluted SF₆ with nitrogen instead of air using gas. The test condition of C₃F₈ is the same as an example 1. A test result is shown in drawing 7. SF₆ in the reactant gas of a coil inlet port SF₆ in the cracked gas after an amount and alkali absorption cell passage As a result of measuring an amount by the TCD gas chromatograph and searching for cracking severity by the degree type, it is SF₆ in 550 to 700 degree C reaction temperature. Cracking severity was 99% or more. By the decomposition trial of C₃F₈, high conversion was acquired with the reaction temperature of 700 degrees C or more.

[0070]

[Equation 2]

$$\text{分解率} = 1 - \frac{\text{出口のSF}_6\text{量}}{\text{供給したSF}_6\text{量}} \times 100 (\%) \quad \cdots (\text{数2})$$

[0071] (Example 7) The catalyst 4-3 which consists of aluminum and nickel is used for this example, and it is NF₃. It is the result of decomposing. The test condition is the same as an example 6 except having used NF₃ gas of 99% or more of purity. Reaction temperature was made into 700 degrees C. NF₃ in the reactant gas of a coil inlet port NF₃ in the cracked gas after an amount and alkali absorption cell passage As a result of measuring an amount by the TCD gas chromatograph and searching for cracking severity by the degree type, cracking severity was 99% or more. Moreover, cracking severity 700 degrees C or less is shown in drawing 8. At least 400 degrees C are 99.9% of cracking severity. It was obtained.

[0072]

[Equation 3]

$$\text{分解率} = 1 - \frac{\text{出口のNF}_3\text{量}}{\text{供給したNF}_3\text{量}} \times 100 (\%) \quad \cdots (\text{数3})$$

[0073] (Example 8) The catalyst which contains aluminum and Zn aluminum:Zn=85:15 (mol %) by the atomic ratio is used, and they are CF₄, C₄F₈, and CHF₃. It decomposed.

[0074] CF₄ Decomposition is CF₄ of 99% or more of purity. Air was added and diluted in gas, the steam was added further, and it carried out by making a catalyst contact with predetermined reaction temperature. Space velocity is 1,000. It is per hour.

[0075] CF₄ in reactant gas concentration -- about 0.5% it is . A steam is CF₄. The flow rate was adjusted so that it might be about 50 times the gas.

[0076] CHF₃ And decomposition of C₄H₈ was performed similarly.

[0077] The test result of drawing 9 is shown. The catalyst which consists of aluminum and Zn shows high decomposition activity also to CHF₃ and CF₄. To C₄F₈, when making it 700-degree-C order or the other temperature, it was shown clearly that high decomposition activity was shown.

[0078]

[Effect of the Invention] According to this invention, decomposition processing of CF4 and the halogenated compound which contains only a fluorine as a halogen like C2F6 can be carried out efficiently.

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to a decomposition processor at the approach and catalyst list which carry out decomposition processing of the compound which contains a fluorine as a halogen like CF4, C2F6, and SF6 and NF3 efficiently at low temperature.

[Translation done.]

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PRIOR ART

[Description of the Prior Art] The fluorine compound gas which contains only a fluorine as a halogen like CF4, C2F6, and SF6 and NF3 is used for the semi-conductor etching agent, the semi-conductor cleaning agent, etc. by the large quantity. However, when these matter was emitted into atmospheric air, it became clear that warming of the earth was caused.

[0003] Gas, such as CF4, C2F6, and SF6, NF3, contains many fluorines (F) as a molecule constituent. Electronegativity of a fluorine is the highest of all elements, and it forms the chemical very stable matter. CF4, C2F6, etc. have the especially strong intramolecular force, and it is the matter lacking in reactivity. It is necessary to heat to an elevated

temperature, and the energy of a large quantity is consumed from this property to decompose by combustion etc. Moreover, the decomposition reaction in an elevated temperature has the large corrosion rate of the equipment ingredient by gas, such as hydrogen fluoride to generate, and the actual condition is that there is no suitable decomposition art.

[0004] As a decomposition art, current and being proposed are the combustion technologies in an elevated temperature. However, in order to use combustible gas, such as a propane, by this approach, it is CO₂ of a large quantity by combustion. And NO_x which is harmful matter generates. Moreover, in order to use combustible gas, such as a propane, there is danger of explosion. Moreover, since it burns at about 1000 degrees C, with the corrosive gas generated by disassembly of a halogenated compound, a furnace wall is damaged, the frequency of a maintenance becomes high, and operation cost becomes large. Therefore, the technique which is low temperature more, and can be decomposed without generating harmful matter is required.

[0005] Although it applies for patents various until now about the decomposition catalyst of a halogenated compound, there are few reports of having disassembled the halogenated compound which contains only a fluorine as a halogen which is object gas of this invention. CF₄ which contains only a fluorine as a halogen although hydrolysis of the halogenated compound by the catalyst containing a titania is indicated by JP,3-66388,A It is described that it receives and resolvability ability is not shown. Moreover, although it tried to hydrolyze CFC-14 (CF₄) using the 2O₃/activated carbon of Fe(s), Okazaki and others was not decomposed as indicated by Chem.Lett.pp(1989).1901-1904. It is extent it is reported about disassembly of the fluorine compound which contains only a fluorine as a halogen that the example using the decomposition agent which becomes JP,7-116466,A from a hydrogen fluoride processing inorganic oxide is.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to this invention, decomposition processing of CF₄ and the halogenated compound which contains only a fluorine as a halogen like C₂F₆ can be carried out efficiently.

[Translation done.]

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] The object of this invention offers CF4, C2F6, the decomposition art that disassembles efficiently the fluorine compound which contains only a fluorine as a halogen like SF6 and NF3 at low temperature, high cracking severity and a decomposition catalyst with a long catalyst life, and a decomposition processor.

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MEANS

[Means for Solving the Problem] this invention persons resulted in this invention, as a result of advancing examination of the decomposition art which is low temperature, and can be efficient, and can disassemble the compound which contains only a fluorine as a halogen like CF4, C2F6, and SF6 and NF3, and corrosion of the equipment by the corrosive gas in cracked gas cannot produce easily to a detail.

[0008] That is, only the fluorine was contained as a halogen, the gas stream which contains this fluorine with a compound with the element chosen from carbon, sulfur, and nitrogen was contacted at the catalyst which comes to contain aluminum under existence of a steam, and about 200-800 degrees C, said fluorine compound was hydrolyzed, and the approach of converting said fluorine compound in a gas stream into hydrogen fluoride was found out.

[0009] CF4 which is object gas, and the halogenated compound which contains only a fluorine as a halogen like C2F6 grade have the property of a fluorine with high electronegativity to the strong intramolecular force, is the reactant scarce matter, and is hardly disassembled at a reaction with oxygen. That is, high cracking severity is acquired only after adding H2O.

[0010] The fluorine compound made into the object of this invention is a halogenated

compound which contains only a fluorine as a halogen. As a constituent of a compound, they are a fluorine, carbon, oxygen, sulfur, nitrogen, etc. As an example of a compound, they are CF₄, CHF₃, CH₂F₂, CH₃F, C₂F₆, C₂HF₅, C₂H₂F₄, C₂H₃F₃, C₂H₄F₂, C₂H₅F, C₃F₈, CH₃OCF₂CF₃, C₄F₈, C₅F₈, SF₆, and NF₃ grade.

[0011] The catalyst which comes to contain aluminum is used in the fluorine compound decomposition art of this invention. aluminum is used in the form of an oxide. Although aluminum can be used independently, it can use combining at least 1 component of Zn, nickel, Ti, Fe, Sn, Pt, Co, Zr, Ce, and the Si. Furthermore, S can be added for these catalysts and the decomposition activity of a catalyst can be raised to them.

[0012] The thing which is the need as catalyst engine performance is having high cracking severity and a long catalyst life. As a result of examining in a detail the catalyst which shows these engine performance, it found out that high resolvability ability could be given with the raw material which also uses 2Oaluminum3 simple substance.

[0013] Cracking severity can be raised rather than the case where aluminum is used independently, by using the catalyst which consists of aluminum and at least 1 component of Zn, nickel, Ti, Fe, Sn, Pt, Co, Zr, Ce, and the Si. In these catalysts, aluminum exists in the state of aluminum 2O₃ or the added metal component, and a multiple oxide. Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, and Si exist in the state of an oxide or a multiple oxide with aluminum. With these catalysts, it is desirable that aluminum is [M] 50-1-mol % at 50-99-mol % for the atomic ratio of aluminum:M (= at least one of Zn, nickel, Ti, Fe, Sn, Co, Zr, Ce, and the Si). or the catalyst which consists of aluminum and Pt -- setting -- Pt -- 0.1 - 2wt% -- containing is desirable. High cracking severity is acquired by making the amount of addition components other than aluminum into said within the limits.

[0014] It is effective in acquiring a long catalyst life to control crystallization of aluminum 2O₃ in a catalyst, and it is desirable to multiple-oxide-ize the metal component which contained nickel, Zn, etc. and was added like NiAl 2O₄ and ZnAl 2O₄, and aluminum. As the approach of the improvement in the catalyst engine performance, the approach of adding S is in a catalyst. The approach of using a sulfate at the time of catalyst preparation, or using a sulfuric acid for it as the addition approach of S, is applicable. S in a catalyst is SO₄. It exists in the form of ion etc. and serves to strengthen the quality of acidity of a catalyst. The amount of S has 0.1 - 20 desirable % of the weight.

[0015] In the decomposition art of this invention, oxygen may be added in the gas stream containing fluorine compounds, such as CF₄ and C₂F₆. It can use for oxidation reaction of CO in cracked gas etc.

[0016] There is the following in the typical reaction of the decomposition reaction of a fluorine compound.

[0017]

CF₄+2H₂O->CO₂+4HF -- (formula 1) C₂F₆+3H₂O->CO+CO₂+6HF -- (formula 2)
CHF₃+H₂O->CO+3HF -- (formula 3) If oxygen exists since the catalyst of this invention also has CO oxidation engine performance although CO generates at the reaction which reaches (formula 3) (formula 2), it will be CO₂ about CO. It can carry out.
[0018] It is necessary to adjust the amount of the steam to add so that a hydrogen molecule equivalent to the F number in the fluorine compound to process at least may exist. Thereby, the fluorine in a compound can be converted into hydrogen fluoride, and

it is made to the gestalt which is easy to carry out after treatment.

[0019] The reaction temperature which hydrolyzes a fluorine compound has desirable about 200-800 degrees C. The reaction temperature in the case of processing the fluorine compound which consists of carbon, a fluorine, and hydrogen at least has desirable about 500-800 degrees C. Degradation of a catalyst is quick, although the rate of superresolution will be obtained if it is used at the elevated temperature beyond this.

Moreover, the corrosion of an equipment ingredient becomes easy to progress. In contacting for a catalyst the gas stream which contains only a fluorine as a halogen and contains this fluorine with a compound with the element chosen from carbon, sulfur, and nitrogen, it is 0.1 - 3vol% to make the content of the fluorine compound in a gas stream into 0.1 - 10vol% desirable still more preferably. Moreover, space velocity is 100 per-hour -10,000. Per hour is desirable still more desirable and it is 100 per-hour -3,000. It is per hour. Space velocity (h-1) is called for in a reactant gas flow rate (ml/h) / the amount of catalysts (ml).

[0020] In the fluorine compound decomposition art by this invention, hydrogen fluoride, a carbon dioxide, etc. generate as a decomposition product. the sulfur oxide of SO₂ and SO₃ grade, and NO and NO₂ etc. -- nitrogen oxides may generate [in addition,] In order to remove these decomposition products, it is desirable for an alkali solution to wash or to wash with water. The approach of washing with water is desirable as an approach of removing hydrogen fluoride, controlling the corrosion of equipment. However, it is desirable to neutralize the water containing hydrogen fluoride with alkali after that in the case of backwashing by water. As alkali, common alkali reagents, such as a water solution of a calcium hydroxide or a sodium hydroxide and slurry liquid, can be used.

[0021] As an aluminum raw material for preparing the catalyst of this invention, the mixture of gamma-alumina, gamma-alumina, and delta alumina etc. can be used. What formed the oxide by baking shows high decomposition activity, using especially boehmite as an aluminum raw material.

[0022] A nitrate, a sulfate, ammonium salt, a chloride, etc. can be used as a raw material of the various metal components for preparing the catalyst of this invention. Nickel nitrate, a nickel sulfate, etc. can be used as a nickel raw material. These hydrates can also be used. Sulfuric-acid titanium, a titania sol, etc. can be used as a Ti raw material.

[0023] The manufacturing method of the catalyst of this invention can use all, such as settling used for manufacture of the usual catalyst, an impregnation method, and the kneading method.

[0024] Moreover, the catalyst in this invention can be used, fabricating it a grain, in the shape of a honeycomb, etc. as it is. As a fabricating method, the approach of arbitration is employable according to the objects, such as an extrusion-molding method, the making tablet fabricating method, and the rolling corning method. Moreover, it can also be used, being able to coat the honeycomb and plate made from a ceramic metallurgy group.

[0025] Although the reactor used in order to enforce the art of this invention is easy to be the thing of the usual fixed bed, the moving bed, or a fluid bed mold, since corrosive gas, such as HF, occurs as decomposition generation gas, it should constitute the reactor from an ingredient which is hard to damage by these corrosive gas.

[0026] The processor used in order to enforce the art of this invention A means to supply nitrogen, air, or oxygen to the means, for example, the gas stream, which adjusts the concentration of the fluorine compound in a gas stream other than the above-mentioned

reactor, A means to heat at least one side in order to contact a gas stream and said catalyst at the temperature of 200-800 degrees C, A means to add a steam or water to said gas stream in order to disassemble said fluorine compound, When said gas stream contacts the catalyst with which said reactor was filled up the generated decomposition product -- water and/, or an alkali water solution -- washing -- some carbon dioxides in this decomposition product, some sulfur oxides of SO₂ and SO₃ grade, NO, and NO₂ etc. -- the exhaust gas cleaning tank from which the part and hydrogen fluoride of nitrogen oxides are removed is provided. It is still more desirable to establish a means to adsorb with an adsorbent etc. the carbon monoxide in said decomposition product which was not removed in the latter part of an exhaust gas cleaning tank, a sulfur oxide, and nitrogen oxides.

[0027] The art of the fluorine compound content gas of this invention is also applicable to an established chip fabrication factory. since there is generally flue-gas-treatment equipment of acid component gas in a chip fabrication factory -- this -- using -- the catalyst of this invention -- CF₄ etc. -- it installs in the exhaust gas line of a fluorine compound, and if a steam is added and heated, decomposition processing of the fluorine compound can be carried out. Moreover, it can move to the location in which the whole equipment or a part of this invention was loaded into the truck etc., and the discarded fluorine compound stuffing bomb is stored, and the contained fluorine compound can also be extracted and processed directly. Moreover, the exhaust gas adsorption tub which adsorbs the circulating pump which circulates through the penetrant remover in an exhaust gas cleaning tank, the carbon monoxide in exhaust gas, etc. may be carried simultaneously. Moreover, a generator etc. may be carried.

[0028] According to the decomposition art of the fluorine compound of this invention, a fluorine compound can be disassembled at low temperature and operation cost can be reduced.

[0029] When processing fluorine compound content gas, the corrosion of the equipment ingredient by acid components, such as HF decomposed and generated, poses a problem, but according to this invention, since the temperature to be used is low temperature, a corrosion rate is small and can decrease the maintenance frequency of equipment.

[0030] The decomposition art of the fluorine compound of this invention consists of an exhaust gas washing process which carries out neutralization clearance of the acid component in the catalytic-reaction process which disassembles a fluorine compound, and decomposition generation gas, and can miniaturize equipment.

[0031] In order to base disassembly of a fluorine compound on a reaction with a steam, its safety as a decomposition art is high, and it does not have danger, such as explosion, like [at the time of using combustible gas].

[0032]

[Embodiment of the Invention] Hereafter, an example explains this invention to a detail further. This invention is not limited only to these examples.

[0033] Drawing 1 shows an example of the decomposition treatment process of the halogenated compound in the case of using at a semi-conductor etching process.

[0034] the inside of the etching furnace decompressed at the etching process -- CF₄ etc. - - a fluorine compound 1 is put in, and it excites for 20 minutes with the plasma, and is made to react with a semi-conductor The inside of a chamber was permuted by N₂ after that, the concentration of a halogenated compound was diluted to several%, and it has

discharged out of an etching furnace by about 10 l/min.

[0035] this emission gas -- air 3 -- adding -- CF₄ etc. -- the halogenated compound was diluted. Nitrogen may be added and diluted at this time. Moreover, nitrogen and oxygen may be added and diluted. The reactant gas 5 which added the steam with the water addition vessel 4 further to this dilution gas is sent to a decomposition process. A decomposition process is performed using the reactor filled up with the catalyst. The concentration of the halogenated compound in reactant gas is about 0.5 - 1%. In a decomposition process, reactant gas 5 is contacted at the catalyst which comes to contain aluminum on condition that space-velocity 1,000 per hour (space velocity (h-1) = a reactant gas flow rate (ml/h) / the amount of catalysts (ml)), and about 200-800 degrees C. In this case, reactant gas may be heated and a catalyst may be heated with an electric furnace etc. Cracked gas 6 is sent to an exhaust gas washing process. At an exhaust gas washing process, the spray of the water 7 is carried out to cracked gas 6, and the exhaust gas 8 with which the acid component in cracked gas was removed is emitted out of a system. The acid wastewater 9 containing a sour gas is processed with a chip fabrication factory existing waste-water-treatment facility. CF₄ etc. -- the cracking severity of a halogenated compound analyzes reactant gas 5 and cracked gas 6 using a FID (abbreviated name of Flame Ionization Detector) gas chromatograph, and a TCD (abbreviated name of ThermalConductivity Detector) gas chromatograph, and asks for them by the material balance of an inlet port and an outlet.

[0036] An example of the processor of this invention is shown in drawing 10. water carries out the spray of the fluorine compound gas from an etching process by the inlet-port spray 10 -- having -- SiF₄ in gas etc. -- an impurity is removed. This gas and the water 7 refined in air 3 and ion-exchange-resin 11 grade are heated at a heater 13 within a preheater 12. A reactor 15 is filled up with the catalyst 14 containing aluminum. Moreover, it had the cooling room 17 which has the spray means 16 of water, and the spray means 18 of water in the latter part of a reactor 15, and it is equipped with the exhaust gas cleaning tank 20 containing a filler 19. Exhaust gas 8 is led by the blower 21 and the acid wastewater 9 is led with a pump 22. In addition, ion exchange treatment is carried out and the water containing the hydrogen fluoride of an exhaust gas cleaning tank can be reused as a pure-water raw material.

[0037] (Example 1) This example is an example which investigated the activity of various fluorine compound decomposition catalysts.

[0038] Air was added and diluted in C₂F₆ gas of 99% or more of purity. To this dilution gas, the steam was added further. The steam supplied pure water to the coil upper part using the micro tube pump, and made it gasify by about 0.2 ml/min. C₂F₆ concentration in reactant gas was about 0.5%. The catalyst and space velocity 2,000 which warmed this reactant gas from the coil exterior to predetermined temperature with the electric furnace It was made to contact in per hour.

[0039] A coil is a coil with a bore of 32mm made from Inconel, has the catalyst bed in the center of a coil, and has the pyrometer tube with an outer diameter of 3mm made from Inconel inside. Bubbling of the decomposition generation gas which passed the catalyst bed was carried out into the calcium-fluoride solution, and it was emitted out of the system. The cracking severity of C₂F₆ was searched for by the degree type by the FID gas chromatograph and the TCD gas chromatograph.

[0040]

[Equation 1]

$$\text{分解率} = 1 - \frac{\text{出口のハロゲン化合物}}{\text{供給したハロゲン化合物}} \times 100 (\%) \quad \cdots (\text{数1})$$

[0041] The method of preparation of each catalyst with which the trial was presented in the above-mentioned conditions below is shown.

[0042] Catalyst 1; commercial boehmite powder was dried at 120 degrees C for 2 hours. It is 0.5 at 300 degrees C in 200g of this desiccation powder. Time amount baking was carried out, and further, burning temperature was raised to 700 degrees C, and was calcinated for 2 hours. The obtained powder was put into metal mold and compression molding was carried out by the pressure of 500 kgf/cm². A cast is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst after completion consists of aluminum 2O3.

[0043] Catalyst 2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 85.38g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Zn=91:9 (mol %) in the atomic ratio. This catalyst contains the multiple oxide of ZnAl 2O4 other than aluminum oxide and Zn oxide.

[0044] Catalyst 3; commercial boehmite was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 50.99g of nickel-sulfate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:nickel=91:9 (mol %) in the atomic ratio. This catalyst contains aluminum oxide, nickel oxide, the multiple oxide of NiAl 2O4, and an S acid ghost.

[0045] Catalyst 4; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 125.04g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:nickel=91:9 (mol %) in the atomic ratio. This catalyst contains aluminum oxide, nickel oxide, and the multiple oxide of NiAl 2O4.

[0046] Catalyst 5; commercial boehmite powder was dried at 120 degrees C for 1 hour. 300g of this desiccation powder, 354.4g of 30% sulfuric-acid titanium solutions It kneaded adding about 300g of pure water. It dried at 250-300 degrees C after kneading for about 5 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Ti=91:9 (mol %) in the atomic ratio.

[0047] Catalyst 6; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 115.95g of iron nitrate 9 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst

presentation after completion was aluminum:Fe=91:9 (mol %) in the atomic ratio.

[0048] Catalyst 7; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is the 95.43g of the second tin hydrates of chlorination. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Sn=91:9 (mol %) in the atomic ratio.

[0049] Catalyst 8; commercial boehmite powder was dried at 120 degrees C for 1 hour. To 200g of this desiccation powder, the water solution which diluted 22.2g (Pt concentration 4.5wt%) of dinitrodiammine Pt(II) nitric-acid solutions with 200ml of pure water was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst after completion is Pt to 2O₃100 % of the weight of aluminum 0.68 weight % It contained.

[0050] Catalyst 9; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 125.87g of cobalt nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Co=91:9 (mol %) in the atomic ratio.

[0051] Catalyst 10; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 76.70g of zirconium nitrate 2 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Zr=91:9 (mol %) in the atomic ratio.

[0052] Catalyst 11; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 124.62g of cerium-nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Ce=91:9 (mol %) in the atomic ratio.

[0053] Catalyst 12; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 20wt% silica sol 129.19g. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. The trial was presented as a particle size. The catalyst presentation after completion was aluminum:Si=91:9 (mol %) in the atomic ratio.

[0054] A test result with a reaction temperature [of the above-mentioned catalysts 1-12] of 700 degrees C is shown in drawing 2 . The decomposition activity of the catalyst which consists of a catalyst which consists of aluminum and Zn, and aluminum and nickel towers otherwise and is high. Subsequently, the decomposition activity of the catalyst which consists of aluminum and Ti is high. It is considered to be the effectiveness of S that a catalyst 3 has high activity rather than a catalyst 4.

[0055] (Example 2) This example is the result of preparing the catalyst to which the presentation of aluminum and nickel was changed using the same aluminum raw material as the catalyst 4 of an example 1, and nickel raw material, and investigating the decomposition activity of C2F6.

[0056] Catalyst 4-1; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 8.52g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=99:1 (mol %) in the atomic ratio.

[0057] Catalyst 4-2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 300g of this desiccation powder, it is 66.59g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=95:5 (mol %) in the atomic ratio.

[0058] Catalyst 4-3; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 210.82g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=80:20 (mol %) in the atomic ratio.

[0059] Catalyst 4-4; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 361.16g of nickel nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=70:30 (mol %) in the atomic ratio.

[0060] Catalyst 4-5; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 562.1g of nickel nitrate 6 hydrates. It mixed, and it kneaded, adding water. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:nickel=60:40 (mol %) in the atomic ratio.

[0061] C2F6 concentration was made into 2% for the activity of a catalyst 4 and a catalyst 4-1 to the catalyst 4-5, and it investigated by the same approach as an example 1 except having made the amount of the pure water to supply into about 0.4 ml/min. The cracking severity 6 hours after test initiation is shown in drawing 3. When mol % of nickel/(nickel+aluminum) is 20 -30-mol %, activity is the highest, and subsequently to the 5-40-mol time of %, activity is high.

[0062] (Example 3) This example prepares the catalyst to which the presentation of aluminum and Zn was changed using the same aluminum raw material as the catalyst 2 of an example 1, and Zn raw material, and investigates activity.

[0063] Catalyst 2-1; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 215.68g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for

about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=80:20 (mol %) in the atomic ratio.

[0064] Catalyst 2-2; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 200g of this desiccation powder, it is 369.48g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=70:30 (mol %) in the atomic ratio.

[0065] Catalyst 2-3; commercial boehmite powder was dried at 120 degrees C for 1 hour. In 126.65g of this desiccation powder, it is 96.39g of zinc nitrate 6 hydrates. The melted water solution was added and kneaded. It dried at 250-300 degrees C after kneading for about 2 hours, and calcinated at 700 degrees C for 2 hours. A baking object is ground and sifted out and it is 0.5 to 1 mm. It considered as particle size. The catalyst presentation after completion was aluminum:Zn=85:15 (mol %) in the atomic ratio.

[0066] C₂F₆ concentration was made into 2% for the activity of a catalyst 2 and a catalyst 2-1 to the catalyst 2-3, and it investigated by the same approach as an example 1 except having made the amount of the pure water to supply into about 0.4 ml/min. The cracking severity 6 hours after test initiation is shown in drawing 4. Activity is the highest when mol % of nickel/(nickel+aluminum) is 10 -30-mol %.

[0067] (Example 4) This example is the result of changing reaction temperature and performing decomposition of CF₄, CHF₃, and C₂F₆. A test condition is space velocity 1,000. It is the same as that of an example 1 except having considered as per hour and having diluted the halogenated compound with nitrogen instead of air. The catalyst used the catalyst 4-3 in an example 2. The result of the trial with each reaction temperature is shown in drawing 5. The catalyst which consists of aluminum and nickel has high decomposition activity also to CHF₃ and CF₄. Moreover, to these fluorine compounds, it has activity even with the low high temperature of about 600 degrees C, and is especially CHF₃. It received, and when CHF₃ concentration in reactant gas was 0.1%, at least 300 degrees C decomposed 35%.

[0068] (Example 5) This example is the result of investigating the effect of the steam in decomposition of C₂F₆. A test condition is space velocity 1,000. Except having considered as per hour, it is the same as that of an example 1. The catalyst made reaction temperature 700 degrees C using the catalyst 4 in an example 1. The trial supplied the steam 2 hours after reaction initiation, and suspended supply of a steam after that. It was begun again to supply a steam 5 hours after. The result of a trial is shown in drawing 6. Cracking severity increased at the time of addition of a steam, and decomposition of C₂F₆ became clear [being based on hydrolysis].

[0069] (Example 6) This example is the result of performing SF₆ and decomposition of C₃F₈ using the catalyst 4-3 which consists of aluminum and nickel. SF₆ A test condition is SF₆ of 99% or more of purity. It is the same as that of an example 1 except having considered as space-velocity 1,000 per hour, and having diluted SF₆ with nitrogen instead of air using gas. The test condition of C₃F₈ is the same as an example 1. A test result is shown in drawing 7. SF₆ in the reactant gas of a coil inlet port SF₆ in the cracked gas after an amount and alkali absorption cell passage As a result of measuring an amount by the TCD gas chromatograph and searching for cracking severity by the

degree type, it is SF₆ in 550 to 700 degree C reaction temperature. Cracking severity was 99% or more. By the decomposition trial of C₃F₈, high conversion was acquired with the reaction temperature of 700 degrees C or more.

[0070]

[Equation 2]

$$\text{分解率} = 1 - \frac{\text{出口のSF}_6\text{量}}{\text{供給したSF}_6\text{量}} \times 100 (\%) \quad \cdots (\text{数2})$$

[0071] (Example 7) The catalyst 4-3 which consists of aluminum and nickel is used for this example, and it is NF₃. It is the result of decomposing. The test condition is the same as an example 6 except having used NF₃ gas of 99% or more of purity. Reaction temperature was made into 700 degrees C. NF₃ in the reactant gas of a coil inlet port NF₃ in the cracked gas after an amount and alkali absorption cell passage As a result of measuring an amount by the TCD gas chromatograph and searching for cracking severity by the degree type, cracking severity was 99% or more. Moreover, cracking severity 700 degrees C or less is shown in drawing 8. At least 400 degrees C are 99.9% of cracking severity. It was obtained.

[0072]

[Equation 3]

$$\text{分解率} = 1 - \frac{\text{出口のNF}_3\text{量}}{\text{供給したNF}_3\text{量}} \times 100 (\%) \quad \cdots (\text{数3})$$

[0073] (Example 8) The catalyst which contains aluminum and Zn aluminum:Zn=85:15 (mol %) by the atomic ratio is used, and they are CF₄, C₄F₈, and CHF₃. It decomposed.

[0074] CF₄ Decomposition is CF₄ of 99% or more of purity. Air was added and diluted in gas, the steam was added further, and it carried out by making a catalyst contact with predetermined reaction temperature. Space velocity is 1,000. It is per hour.

[0075] CF₄ in reactant gas concentration -- about 0.5% it is . A steam is CF₄. The flow rate was adjusted so that it might be about 50 times the gas.

[0076] CHF₃ And decomposition of C₄H₈ was performed similarly.

[0077] The test result of drawing 9 is shown. The catalyst which consists of aluminum and Zn shows high decomposition activity also to CHF₃ and CF₄. To C₄F₈, when making it 700-degree-C order or the other temperature, it was shown clearly that high decomposition activity was shown.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is drawing showing the treatment process of the example 1 of this invention.

[Drawing 2] It is drawing showing the engine performance of each catalyst of this invention.

[Drawing 3] It is drawing showing the C2F6 resolvability ability of the aluminum-nickel catalyst of this invention.

[Drawing 4] It is drawing showing the C2F6 decomposition activity of the aluminum-Zn catalyst of this invention.

[Drawing 5] It is drawing showing C2F6 of the aluminum-nickel catalyst of this invention, and the decomposition activity of CHF3 and CF4.

[Drawing 6] It is drawing showing the effect of the steam in C2F6 decomposition of the aluminum-nickel catalyst of this invention.

[Drawing 7] It is drawing showing SF6 of the aluminum-nickel catalyst of this invention, and the decomposition activity of C3F8.

[Drawing 8] NF3 of the aluminum-nickel catalyst of this invention It is drawing showing decomposition activity.

[Drawing 9] CF4 of the aluminum-Zn catalyst of this invention, C4F8, and CHF3 It is drawing showing decomposition activity.

[Drawing 10] It is the outline block diagram of the decomposition processor by one example of this invention.

[Description of Notations]

1 --CF4 etc. -- a fluorine compound and 2 -- N2, 3 -- air, and 4 -- water addition machine
-- 5 [-- Exhaust gas, 9 / -- Acid wastewater,] -- Reactant gas, 6 -- Cracked gas, 7 --

Water, 8 10 [-- A heater, 14 / -- A catalyst, 15 / -- 16 A reactor, 18 / -- A spray means, 17
/ -- A cooling room, 19 / -- A filler, 20 / -- An exhaust gas cleaning tank, 21 / -- A blower,
22 / -- Pump.] -- An inlet-port spray, 11 -- Ion exchange resin, 12 -- A preheater, 13

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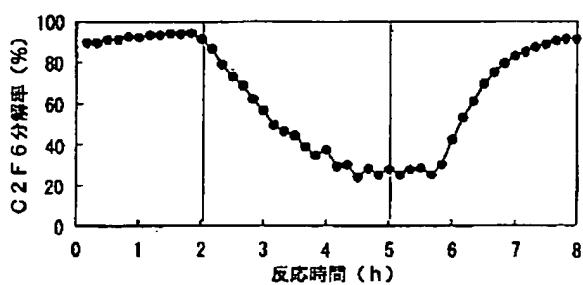
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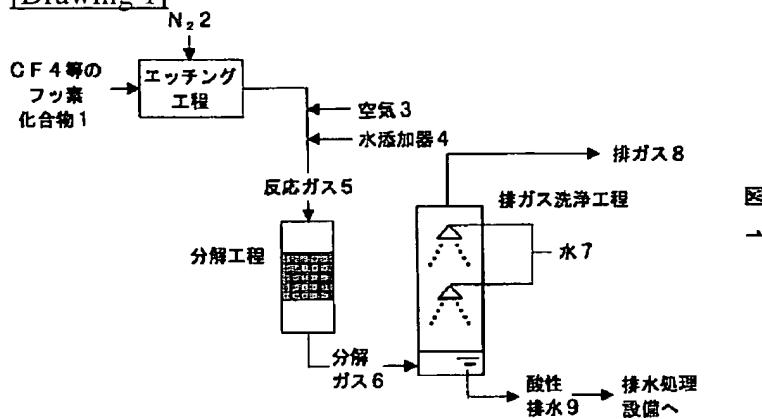
DRAWINGS

[Drawing 6]

図 6

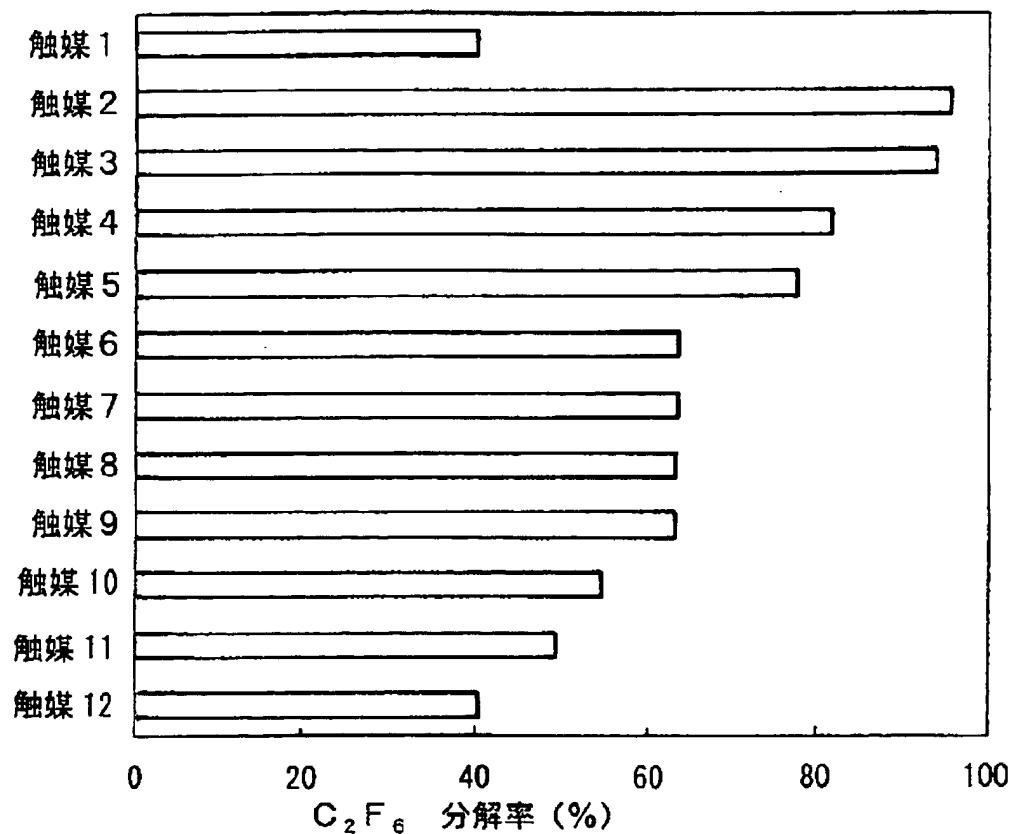


[Drawing 1]



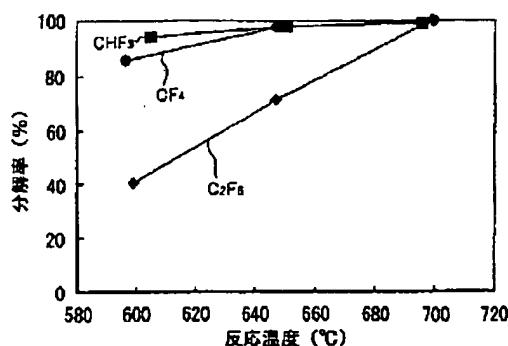
[Drawing 2]

図 2



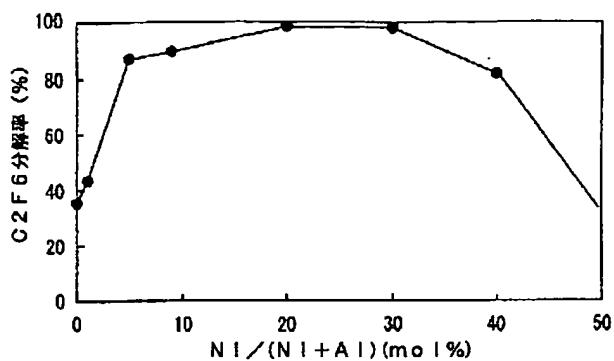
[Drawing 5]

図 5



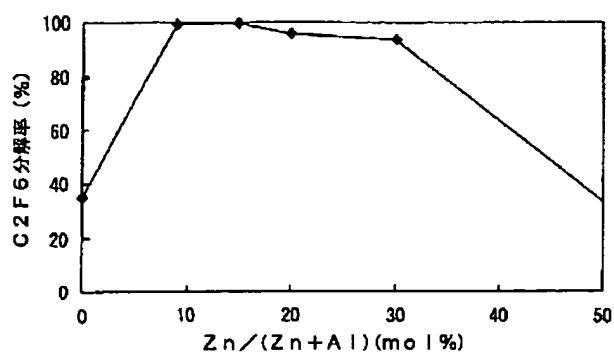
[Drawing 3]

図 3



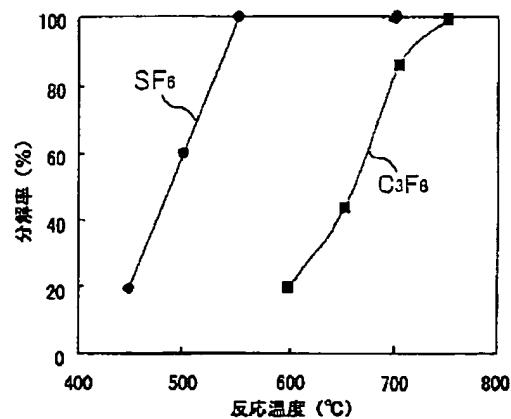
[Drawing 4]

図 4



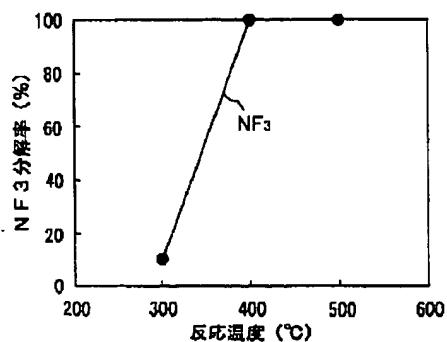
[Drawing 7]

図 7



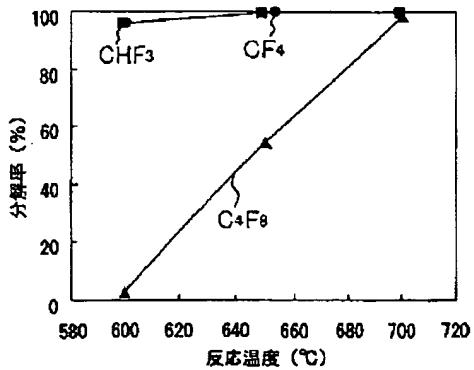
[Drawing 8]

図 8

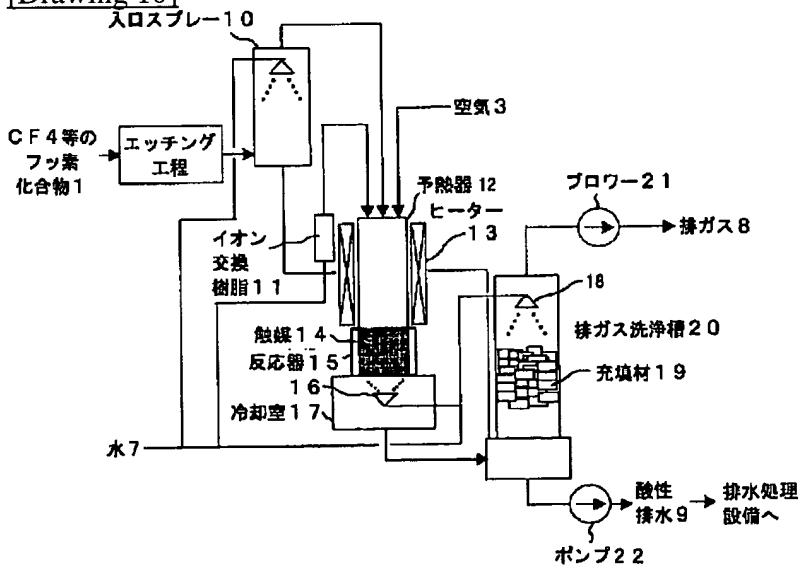


[Drawing 9]

図 9



[Drawing 10]

図
10

[Translation done.]